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THE CHLORINE CELL INSTALLATION OF THE MONTREAL WATER AND POWER COMPANY[1]

By F. H. Pitcher and James O. Meadows

The sterilization of public water supplies with chlorine or chlorine compounds, either as an adjunct of filtration or as a sole method of purification, is now standard practice, and this method is well understood, but the production of electrolytic chlorine and the application of the gas, so produced, to the water to be purified is of rather recent date, and, except in a general way, is but little understood by the water works fraternity. The electrolytic cell installation of the Montreal Water and Power Company has been in service since the first part of the present year, a period hardly long enough from which to gather average operating results, but during the time that the plant has been in service considerable information and data have been secured that are of interest.

HISTORICAL SKETCH

The fact that common salt can be broken down or decomposed into its elements, sodium and chlorine, by electrolysis, has been known practically since the discovery of the galvanic cell, but the commercial application of this principle was impossible until the dynamo was developed, and even after this was accomplished, many difficulties had to be overcome to perfect an electrolyzing equipment which would efficiently and effectually separate the products and at the same time withstand the corrosive action of the chlorine gas. Numerous types of electrolytic cells, or decomposing chambers, have been evolved and perfected to a degree, but only a few have been even a partial success commercially.

In its simplest form an electrolytic chlorine cell is a tank or chamber, composed of materials that will resists chlorine and containing brine in which a positive and a negative electrode are immersed. Upon the passage of an electric current through the cell, chlorine gas is liberated at the positive electrode, or the anode, and simultaneously metallic sodium is released at the negative electrode, or the cathode. This metallic sodium immediately combines with the water in the brine, forming caustic soda and liberating hydrogen gas. The momentary products from the cell are, therefore, chlorine gas, a weak caustic solution, and hydrogen gas; but the chlorine gas and the caustic soda immediately combine to form sodium hypochlorite or so-called sodium bleach. Cells of exactly the type described have been and are now sold for laundry use, but they cannot be employed when a complete separation of the products is required. Furthermore, this type of cell can produce only a weak bleaching solution, and that inefficiently, because after the sodium hypochlorite reaches a certain strength, it is in turn decomposed by the electric current, making the process retroactive with the damaging result that the oxygen in the sodium hypochlorite combines with the carbon of the anodes to form carbon dioxide gas.

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[1] Read before the Chemical and Bacteriological Section at the Richmond Convention, May 10, 1917.

From the foregoing it is obvious that to obtain a perfect cell for the production of chlorine gas, the chlorine and the caustic soda which are the primary products of electrolysis must be prevented from recombining. To secure this separation of the products, four distinct lines of development have been followed:

1. By the insertion of a permeable diaphragm between the anode and the cathode.
2. By employing a mercury cathode which is alternately the cathode in the electrolyzing compartment of the cell and the anode in an adjoining compartment where the amalgam of metallic sodium and mercury is decomposed by water.
3. By placing the cathode under the anode and depending upon the stratification of the electrolyte which occurs due to the different densities of the brine solution and the caustic solution surrounding the immersed cathode.
4. By the use of a fused salt electrolyte and a molten lead cathode.

Only the mercury and the diaphragm type have survived commercial exploitation in this country on account of the inefficiency and cost of maintenance of types 3 and 4.

The several forms of diaphragm cells which have been commercially operated consist of two groups:

a. Cells with submerged diaphragms and cathodes.

b. Cells in which the electrolyte comes in contact with one face only of an unsubmerged diaphragm.

Very early in the history of electrolysis, Le Sueur, Gibbs, Crocker, Nelson and others conceived and operated cells of the submerged diaphragm or first group. Le Sueur employed a horizontal diaphragm and Gibbs employed a circular cell with a vertical diaphragm.

The unsubmerged diaphragm group is in turn subdivided into the two classes of permeable and impermeable diaphragms.

All of the permeable diaphragms for both the unsubmerged and the submerged group of cells are composed of asbestos paper or cloth, disposed in the cell in such a manner than they separate it into two distinct compartments, designated as the anode compartment, into which the saturated brine is introduced and where the chlorine is formed, and the cathode compartment, where the caustic soda is formed.

With cells of the submerged diaphragm group it is possible to a large extent to keep the chlorine gas and the caustic soda separated by maintaining a liquor level in the anode compartment higher than the level in the cathode compartment, thus inducing a continuous flow from the anode to the cathode chambers. Nevertheless, by osmotic action and mechanical interchange through the diaphragm, the salt caustic liquor from the cathode compartments invades the anode compartment and there combines with the chlorine to form sodium hypochlorite, which results in the loss of these two products and causes a rapid disintegration of the anode, as previously noted in the description of the laundry cell.

Cells of the submerged diaphragm type operate in practical service at not more than 85 per cent current efficiency (excepting only the Billiter-Siemens cell), with a maintenance which is in direct ratio to their lack of efficiency, because the less efficient the cell, the more hypochlorite is formed in the anode compartment with the consequent shortening of the life of the anodes.

Cells of the submerged diaphragm type operate with reasonable efficiency during the first few weeks of service after a new diaphragm has been inserted, but as the age of the diaphragm increases, it becomes less permeable and accordingly more effective as an osmotic vehicle for the contamination of the anode by the products of the cathode compartments.

With cells of the second group having the diaphragm immersed on one side only, the above described contaminating influences are entirely eliminated, because there is no large body of caustic liquor present in the cathode compartments since the cathode liquor is withdrawn as fast as it is formed. It follows that in actual service, cells of this type closely approximate theoretical current efficiency with a resulting increased output and a longer life than can possibly be attained by cells of the submerged diaphragm type.

The Allen-Moore cell as installed by the Montreal Water and Power Company is of the unsubmerged diaphragm type and is guaranteed to have a current efficiency of not less than 92 per cent.

DESCRIPTION OF THE INSTALLATION

The chlorine cell installation consists of the following main parts; a salt storage bin having a capacity of 40 tons of salt, the brine saturating and purifying equipment, two 15-horse-power motor-generator sets, four chlorine cells, and the silver ejectors and distributing lines for applying the chlorine water to the water to be treated.

The brine saturating and purifying equipment consists of the following parts; three vertical galvanized iron saturators, 27 inches in diameter by 6½ feet in height, provided with a spray system at the bottom and an outlet 6 inches from the top; two concrete reaction tanks having a capacity of 82 cubic feet each. These tanks are built with sloping bottoms and are provided with a pipe grid for air agitation. Two sand filters are provided for filtering the purified brine, which passes from the filters to the two concrete storage tanks having a capacity of 276 cubic feet each.

The distributing lines for applying the chlorine water to the water to be treated are 1-inch chemical hose lines, and the chlorine gas is injected into the water by means of a silver ejector, which maintains a 4-inch vacuum on the chlorine cells and takes the gas from the chlorine main through the ejector to the distributing lines.

Each of the four electrolytic cells is a standard 600-ampere unit and is 7 feet long by 20⅝ inches wide. Each cell is provided with Atcheson graphite anode plates, and pure wrought iron perforated cathode plates. As stated previously the Allen-Moore cell is of the unsubmerged diaphragm type and uses asbestos paper for the diaphragm material. Unlike several other types of electrolytic chlorine cells, the cell box is made of concrete, properly protected at the surface to withstand the action of the chemicals.

The cells are connected in series and are provided with short-circuit switches or cut-outs. The voltage carried on each cell is approximately 3.3 volts, and each cell is capable of producing 32 pounds of chlorine per twenty-four hours.

To prepare the brine solution, a small quantity of water under pressure is allowed to flow in at the bottom of the saturators. The saturators being charged with salt, a saturated solution of salt is delivered to the two concrete reaction tanks. A sufficient quantity of soda ash is added to the brine in the reaction tanks to combine with the calcium and magnesium salts present in the brine, and the contents of the tanks are agitated for one-half hour to insure complete mixing of the soda ash solution with the brine, and also to hasten the reaction. The solution is then allowed to remain in a

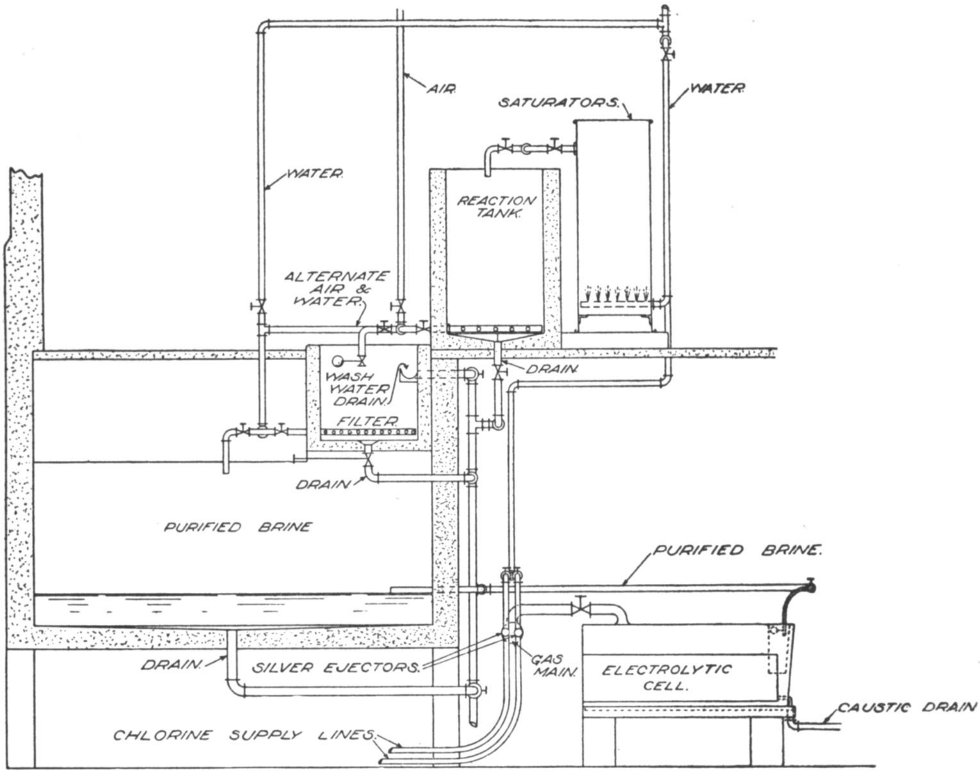

FIG. 1. BRINE SATURATING AND PURIFYING EQUIPMENT

quiescent state for one hour to allow the precipitate formed to settle, when the solution is filtered through the sand filters into the purified brine storage tanks. A sample of the purified brine is taken and titrated for residual alkalinity, which determines the amount of hydrochloric acid necessary to add to neutralize the alkalinity and leave a residual acidity of about 0.01 per cent. It is necessary to have the electrolyte slightly acid to prevent the formation of hypochlorites within the cell, and the subsequent loss of cell efficiency.

The cell or current efficiency is computed from the cell flow of caustic liquor, the amount of caustic produced, and the current used to effect the dissociation. The flow of caustic liquor is measured for a certain period and computed as liters flow per hour,and at the same time a portion of the caustic liquor is titrated with normal acid to determine its strength. Knowing the flow per hour and the amount of caustic per liter the number of grams of NaOH produced per hour can be easily determined, which figure is known as the actual caustic production.

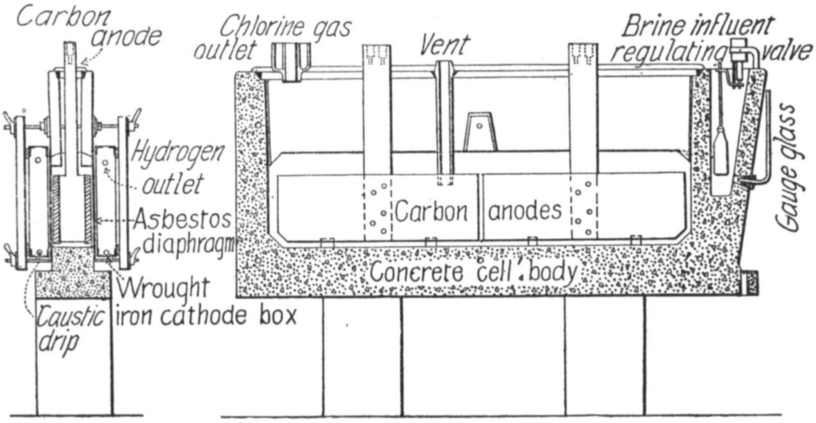

FIG. 2. SECTIONS OF CELL USED AT MONTREAL

The number of amperes passing through the cell multiplied by 1.49 grams (theoretical NaOH production per hour per ampere) will give the theoretical caustic production, and this result, when used as the divisor, and the actual caustic production as the numerator will give a product which, when multiplied by 100, will be the percentage current efficiency of the cell. Also as the amount of caustic produced is to the amount of chlorine produced as the atomic weight of NaOH is to the atomic weight of chlorine, the amount of chlorine produced can be easily determined. The amount of chlorine produced can also be determined by direct titration, and this chlorine assay will act as a check on the first determination. The average operating current efficiency of the cells has been maintained so far at about 93 per cent.

COST OF CHLORINE PRODUCTION

Annual cost of producing 90 pounds of chlorine per day or 32,850 pounds per year

Salt at $8.00 per ton, delivered	$500.00
Power, 15 H.P., at $30.00, flat rate	450.00
Labor and superintendence	500.00
Interest at 6 per cent on capital cost	300.00
Depreciation, 15 per cent	750.00
Total	$2,500.00

Three out of the four chlorine cells furnish the requisite amount of chlorine for sterilization, yielding 90 pounds of chlorine gas per twenty-four hours or 32,850 pounds per year, making the cost of chlorine produced 7.6 cents per pound.

The annual cost of sterilization previous to the installation of the chlorine cells was as follows:

Chloride of lime at 3.75 cents per pound	$4,105.00
Interest at 6 per cent	150.00
Depreciation at 5 per cent	125.00
Labor and superintendence	500.00
Total	$4,880.00

As the amount of chloride of lime required was 300 pounds per day or 100 pounds of available chlorine, the cost per pound was 13.4 cents, or 5.8 cents per pound more than chlorine produced by the electrolytic cells.

With normal market conditions the annual cost of the two forms of treatment would be approximately the same, if one did not consider the general depreciation that chloride of lime causes about a water purification plant.

OPERATION

An electrolytic chlorine cell functions at its best when under a constant current load, and for this reason it is good practice not to vary the load, or if varied to bring about the change gradually. Variations in load cause a considerable deterioration of the diaphragms, with a consequent loss in cell efficiency. For this reason automatic control of the chlorine production from an electrolytic cell is not practical, and for the treatment of a large volume of water, without appreciable variations in volume, automatic control is not required, for the dosage can be regulated for the maximum requirements without causing tastes or odors during the minimum consumption periods. The three cells required to supply the chlorine consumed for sterilization are operated with a current load of 500 amperes and 13 volts. The electrolytic cells require very little attention and up to date have given excellent satisfaction.

The caustic liquor from the cells contains about 12 per cent of sodium chloride and about 10 per cent of NaOH. No recovery of the salt and caustic is attempted, because the amounts of these two chemicals produced are so relatively small that their recovery would not be economical. For large installations the recovery of the salt and caustic is a regular feature of the process, the salt recovered being used over again, and the caustic is concentrated and sold as liquid caustic.

CONCLUSIONS

The chlorine cell installation was adopted because of the saving effected over the present high price of chloride of lime and inability to secure this chemical with any degree of certainty, and also because common salt is very much easier to handle around a water purification plant, and its use in the chlorine cells does not cause the general deterioration about the works that the use of chloride of lime does. Over-dosage with chlorine does not cause the trouble that chloride of lime over-dosage does, because odors and tastes are not present to the same degree.

The short experience at Montreal with chlorine cells for the sterilization of a public water supply indicates that an installation of this kind is perfectly feasible for large water supplies where the cost of power is not excessive.

DISCUSSION

S. B. Applebaum: The paper suggests an economical application of the used brine solution from the regeneration of permutit water softening filters. This regeneration consists in passing a solution of brine slowly through the zeolite during the night. This brine leaves the filter just as clear as when it entered and the latter half of the brine is sufficiently free from calcium and magnesium chlorides to be entirely suitable for electrolytic purposes. There are several textile mills employing the used brine solution in this way, applying the resulting sodium hypochlorite for bleaching.

In a municipal pumping station where a permutit plant is used to keep scale and mud out of the boilers, the used brine liquor is electrolyzed and the sodium hypochlorite is sold to a hospital as a disinfectant. The receipts from these sales pay for most of the operating costs of the softening plant. The paper suggests the possibility of operating permutit plants in pumping stations by using the brine electrolytically as part of the sterilization process.

Mayo Tolman: The water supplies of a few West Virginia towns are disinfected by electrolytic bleach manufactured by the so-called Hargraves-Bird process, controlled in this country by the West Virginia Pulp and Paper Company. Each cell is 10 feet long, 5 feet deep and 15 inches wide. It is fitted with six anodes and two cathodes. The anodes consist of copper bars into which are leaded six carbon rods 2 inches in diameter, which are embedded in neat cement until but an inch of the rods projects on either side. Two-inch holes are drilled through disks of crucible carbon which are forced over the ends of the rods, giving a much greater area of contact of the carbon with the brine solution in the cell. These anodes, which weigh about 400 pounds apiece, are suspended in the center of the cell from a busbar that extends overhead. The cathodes consist of thin sheets of ground asbestos and cement, backed by perforated copper plates. They are of such size as to cover the entire sides of the cell, to which they are clamped by arched cover plates.

A steady stream of brine of a specific gravity of 2.6 Baumé, is introduced into the cell, where it is broken down into sodium and chlorine by an electric current of $4\frac{3}{7}$ volts and 27 amperes. The sodium passes through the diaphragm formed by the cathodes and is treated with steam and carbon dioxide, forming sodium carbonate, used in the paper industry. The chlorine is sucked by powerful fans upward through towers of terra cotta pipe into which lime water is sprayed. The bleach liquor or chlorine water thus formed contains about 19.5 parts of available chlorine to the liter; that is, 55 gallons of the liquor is approximately equal to 24 pounds of 37 per cent hypochlorite of lime in the solid form. The liquor is readily handled in special bronze pipes and is a very excellent disinfectant for water sterilization purposes. In fact, on a number of rather extensive tests it has been found, part per part of available chlorine, to be far superior to the hypochlorite of lime prepared from the solid.